

NICKEL ELECTRODE PLATE THICKENING STUDY

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I would like to begin by saying that this paper will be given in two parts. The first part I will be presenting, and the second part will be given by Dean Maurer.

I would like to report on the interim results of a study on the rate of thickening of the nickel electrode.

One of the generally accepted failure modes of geosynchronous nickel-cadmium batteries is capacity loss, high resistance from shorts caused by excessive separator compression resulting from the thickness growth of the nickel electrode with cycling.

Until recently, little or no information existed on the effect of various operational parameters on the rate of this process. This multivariate study of individual electrodes was undertaken to determine some of these effects under geosynchronous type of conditions in support of the AT&T/GT&E satellite programs with COMSTAR and follow-on systems. To date, 36 combinations have been measured long enough to see trends.

This paper describes preliminary results on temperature, electrolyte composition, manufacturing lot, cycle parameters, and reconditioning methods. Let me tell you a little bit about the experimental procedure.

The plates were cut to 1.5 by 1.5 inches and cycled with large cadmium counter electrodes in specially designed lucite flooded cell containers to prevent fringe field effects.

The holders were filled with the appropriate electrolyte to a level slightly above the electrodes. A thin layer of high-purity mineral oil was floated on the surface of the solution to retard evaporation and the formation of carbonate. The cells were cycled in series and received constant current charge and discharge.

Individual diode protection networks were used for low voltage cut out to bypass the discharge current when cell voltage reached approximately 0.6 of a volt.

(Figure 6-1)

Table I is an outline and description of each of the variables investigated. The variables will be temperature, manufacturing lot, electrolyte composition, and test regime.

The first three temperatures we used were zero, room temperature, and 45°C. The cells that were at room temperature were exposed to controlled room temperature which was 23°C, plus or minus two degrees.

The ones at 0°C and 45°C were cycled in temperature cabinets that were maintained at approximately plus or minus one degree Centigrade.

The electrodes used in this study were BTL electrochemically deposited plates and General Electric chemically deposited plates. The BTL electrodes were made from the same sinter lot using nickel screen substrate and impregnated in-house. They were approximately 20 mils thick. The General Electric electrodes were all of the type used in COMSTAR, which was the PQ type and contained perforated sheet substrates which was nickel plated iron. They were approximately 27 mils thick.

Lots 9 and 12 were taken from COMSTAR, and lot 9 and lot 12 cells had gone through qualification testing. Lot 19 positives were approved electrode samples from a recent build of COMSTAR cells but had not actually been assembled into the cells.

All the GE plates were made by the CD process. There were five electrolyte compositions tested. You see the 30 percent KOH and 20 percent KOH used because they typify the range of concentration which may be found in sealed cells.

CO₃ was actually a solution of 3.5-molar potassium hydroxide and 1.8-molar potassium carbonate. This was included to simulate the effect of nylon degradation products from the separator.

K/Na was a solution of 50 percent 7-molar potassium hydroxide and 50-percent sodium hydroxide. It has been a consideration to add sodium to the electrolyte to improve charge efficiency at high temperature, and we examined its effect on rate of thickening.

An additional electrolyte not included in this summary was a solution of nylon which we hydrolyzed at 200°F and 30 percent KOH. The cell gave no capacity when cycled, and unfortunately there was insufficient data to include this in the population.

The last variable was test regime. Tests 1A and 1B were at C/6 charge rate. Test 2A was C/20 charge rate all for 110 percent returned; test 3A was a dual charge consisting of C/6 for 3 hours, 58 minutes. This was also 110 percent charge returns followed by C/30 trickle charge for 6 hours, 50 minutes. The latter is more typical of cycles seen in geosynchronous orbit.

All tests received standard C/2 discharges to 60-percent depth. The cells were continuously cycled according to their test regime for 12 days, which was about 50 cycles, to simulate an eclipse season.

After each eclipse season, all groups were fully discharged and given a reconditioning cycle. The 1A, 2A, and 3A groups received a C/40 discharge to 0.6 of a volt.

Group 1B differed only in its reconditioning cycle which involved repetitive discharge at C/40 for 8 hours, followed by 16 hours of open circuit until it reached again 0.6 of a volt. This is so the cell does not see more than 8 hours of discharge in a 24-hour period.

Following reconditioning, the oil was floated off the surface of the electrolyte, and the electrodes were removed for thickness measurements and visual inspection.

Wet-plate measurements were made in five places with a hand-held micrometer accurate to plus or minus a tenth of a mil. Visual deterioration such as blisters, cracking, flaking was all noted. If the deterioration was advanced, the electrode was replaced. Fresh electrolyte and oil were added after each eclipse season.

The mean thickness for each individual electrode was used to calculate a percentage thickness increase and a typical result is shown in Figure 6-2.

(Figure 6-2)

Percent thickness and cycle number.

A linear regression was done on each set of data points, and at least three eclipse seasons were accumulated in all cases. The slope of the regression line was used for a comparison and analysis discussed next. No attempt has been made at this time to calculate the statistical significance of these comparisons; however, an analysis will be made at the completion of the experimental program and reported later.

Now, as we expected, the BTL electrochemically impregnated electrodes demonstrated overall superiority in all testing conditions and showed no growth within the experimental error up to about 800 cycles. We have gone that far so far.

(Figure 6-3)

This figure shows a comparison with two GE chemically impregnated lots under similar test conditions. The scale on the last one we saw goes below zero, so if you can follow the zero line, that's where the BTL electrode, the slope was almost at zero. The two top lines are the GE plates.

What we generally use to qualify our electrochemically deposit on plates is an accelerated test. I won't go into the description, but Dean is going to give this brief description with some typical results. He will show you that in a few minutes.

(Figure 6-4)

The most surprising results of this study can be seen in this figure, in which, for each electrolyte, the average slope of all other conditions is plotted versus the temperature. The temperature, as you see here, is not monotonic. The growth rate is lowest near room temperature. It gets larger at both higher and lower temperatures.

A more detailed analysis of this effect will be carried out in a later paper. There are probably two mechanisms involved:

Expansion due to forces resulting from density changes between charge and discharge at higher temperature and forces resulting from fluid gas flow in the capillary structure which are controlled by viscosity effects at lower temperature. This effect is probably also responsible for the effect of concentrations of KOH, although the possibility of structure effects cannot be ruled out.

The high rate for carbonate at 45°C is undoubtedly due to corrosion effects. The high rate for the K/Na mixture, the potassium sodium, is probably due to the cation exchange which becomes significant at elevated temperatures with the smaller sodium ions. This is in line with the observed capacity degradation at room temperature, in the electrolyte containing one normal lithium hydroxide. The study has been done.

Another significant result is shown in Figure 6-5.

(Figure 6-5)

Here, we have the average slope for each lot number plotted against the temperature. You can see the lot-to-lot variability is as large as most of the other variables, and clearly indicates the need for an accelerated test and requirements for lot acceptance prior to cell assembly for flight programs still forced to use chemically impregnated plates.

This is especially true for programs requiring faster cycling where plate thickening is more likely to limit life before separator degradation. Clearly electrochemically impregnated plates are the best approach. However, if the process is not properly controlled, extensive growth can still occur as Dean will show with the accelerated test studies.

The effect of the cycle regime has not been studied as extensively as the other variables; however, the effects can be seen by calculating the average ratio of the slopes for relevant sets of conditions.

(Figure 6-6)

Table II shows this ratio at 23°C for the effect of reconditioning methods, 1B and 1A, and the effect of trickle charge, 3A and 1A.

As can be seen, the interrupted reconditioning results in more than 50 percent greater growth than the standard method. No explanation is offered at this time.

The trickle charge period following the standard charge in 3A is seen to result in three times the thickening rate than without it. This probably is due to the same fluid gas flow forces which give rise to the generally higher rates at low temperature. This effect merits further study but indicates that the trickle charge should be minimized, but probably not eliminated due to the danger of cadmium migration.

The problem can be eliminated, of course, on new designs with the electrochemical impregnation.

In conclusion, this study of plate growth leads to the following conclusions insofar as the flooded electrode measurements can be extrapolated to the starved, sealed cell conditions.

A major thing would be BTL electrochemically impregnated electrodes exhibited no growth under any of the conditions tested.

The growth rate of chemically impregnated plates is increased at temperatures both higher and lower than room temperatures, suggesting that satellite battery temperature reduction to minimize separator degradation must be tempered by plate-growth rate considerations.

Lot-to-lot variability in the growth rate of chemically impregnated plates is larger than the effects of most of the other variables.

And last, the effect of trickle charge following the normal charge results in a large increase in thickening rates.

The trickle charge probably should not be eliminated on existing satellites, however, due to the danger of cadmium migration on open circuit. On the other hand, changes in all these problems can be eliminated by using properly prepared electrochemically impregnated electrodes.

MAURER: I was going to talk about an accelerated test method for electrochemical positives; however, after the nomenclature discussion this morning I won't talk about an accelerated test. I am going to talk about a fast test.

(Figure 6-7)

We have been using a test method in the lab for quite a number of years that involves 10C charge and discharge with 100-percent overcharge. 10C was selected simply because it was a convenient number to use, easy to multiply by 10, and we used 100-percent overcharge to get a lot of this rather stressing condition into the evaluation routine. Then we used this on electrochemical electrodes to look at the effects of a number of different variables.

Some of this data was presented by Beauchamp and myself at the 1971 Collector Conference, and I just want to show it here to remind you that it can be used to measure these effects. This is the effect of cobalt concentration on the cycle life plotting capacity versus cycle number for different levels of cobalt which were achieved by simply adding cobalt to the impregnation bath.

Without cobalt the capacity falls off very rapidly. As soon as you get some in, you get greatly improved capacity maintenance, and an additional effect is that the electrodes without cobalt warp and bend a great deal. And with a little bit of cobalt, they remain flat.

Now, we can compare this with something at a somewhat lower rate: the 2C rate.

(Figure 6-8)

Again, there are the same electrode lots showing the same results.

(Overlay)

If I lay these on top of one another, you see the comparison between high and low rate is very close. There is a slight difference here on the 13-percent cobalt line, but this one again would be somewhat in agreement with the results on the accelerated study that was reported this morning.

Charge rates don't have all that big an acceleration factor. But they do allow you to get the information in a hurry.

(Figure 6-9)

This is the same thing on cadmium additive to the nickel electrode. The effect is similar, but doesn't give as good a result as cobalt. I haven't got any data on the combination of cadmium and cobalt both in the electrode.

(Figure 6-10)

This is the effect of lithium in the electrolyte. This work was done by Beauchamp and was published previously at the lab. It shows the effect of capacity with cycle number again at this 10C rate on an electrode with five-percent cobalt and the 32 percent line is up here.

This is a log plot now rather than linear that you saw on previous ones.

So this line is more or less in agreement with the one you saw before, and you put a little bit of lithium in, and you get a big degradation in capacity maintenance.

So one should be careful about adding lithium for these aerospace cells. You tend to cycle them quite a lot.

(Figure 6-11)

Next, with the interest in electrochemical electrodes for their thickening properties, we started using this method to look at that effect. By the way, the setup for this study is more or less the same as what was just described for the chemical plates, except, to handle the very high rates we put them in flooded cells that had a great deal of excess electrolyte. But again, minimizing fringe fields.

We had enough electrolyte in them so that we didn't change the composition significantly for perhaps the longest watering period which would be like a holiday weekend. Then, we put plastic covers over them to minimize the KOH spray they could get. The leads are gold plated alligator clips that have the solder joint protected with shrink tubing to prevent corrosion from taking place.

The capacity, or rather the discharge, is limited by meter relays instead of diodes.

Doing this, then stopping every so often to measure thickness, and looking at electrodes from a variety of sources, you get this kind of data.

(Figure 6-12)

You see, there are really four classes of electrodes here: There is the one we know and love, which doesn't grow at all; some that have a slight growth; some have a sudden growth for a few cycles and then flatten out or nearly flatten out; then another set that have that same thing with some greater increase.

This is really the result of the impregnation process or the sinter not being quite right in each particular case. And Tom O'Sullivan in my group has done some work along this line and has been able to reproduce those effects deliberately.

(Figure 6-13)

This is some of that data.

Basically, the problem is that you have to limit the loading of the electrode to the number that McHenry was talking about, 1.6 grams per cc of void as an average over the plate.

However, you also have to be careful that the active material distribution is uniform. You might have 1.6 grams averaged through the thickness of the plate, but it might be all located near the center. That is near the substrate or it might be all located out near the surface.

If you have those conditions, then you get this kind of an effect. And if you have it simply too high, you get this continual growth kind of an effect. But, if you limit it to a well distributed 1.6, then you get no growth.

The other things you have to watch out for, of course, are big voids in the sinter. The sinter needs to be uniform for distribution.

Now, to compare these high-rate growth rates with what you get at more common conditions, see the following figure.

This is a plot of some of the data that Madeline has just shown from that same study. The upper line represents the high-rate cycling data, and the lower two points here represent data on the same plate, taken from a different place on the same plate, done at the geosynchronous rates that she was talking about. So you get the same kind of slope. The displacement is probably due to measurement errors in the initial thickness measurement.

So the technique can, in fact, be used to get information about the quality of plates. I make no claim that I can compare a 1000- or a 2000-cycle plate from this study, directly to a sealed cell.

In a sealed cell, under some other kind of capacity conditions, I might very well get a different cycle life.

But, what I am saying is that the relative merits of plates on this test are probably carried over into the sealed cell.

I would like to take this opportunity to say one other thing about how this might relate to real life predictions or life mechanisms on geosynchronous batteries and the effects of reconditioning and that sort of thing that we have been discussing.

My view of this, of the voltage profiles that you see from orbital data, is that it involves several classes of things going on in the cell.

(Figure 6-14)

Some of which are visible in the voltage data and some of which are not. If I just plot some quality function, it might be voltage versus time or season in the geosynchronous orbit, I get some band that has this general shape.

It might be a bit flatter with some reconditioning methods, and a bit steeper with others. It is, in general, somewhat reversible, although it has an irreversible component.

(Overlay)

The reversibility part of it is what you really recover by the reconditioning method. But what this doesn't show are the effects of anything else going on in the cell (for example, separator degradation, which will proceed to the point that either the negative is fully charged and the cell blows up, or the separator is gone and it shorts out). And that will be seen in the outside world as a very sudden collapse of cell quality.

So that is going to be a vertical line out here, somewhere.

Then things like plate thickness increase. It will squeeze the separator, and then you will begin to get some degradation.

(Overlay)

So that is going to be a vertical line, but one with a very high slope. Depending on the particular cell design, all of these curves can move back and forth with respect to one another. Certain kinds of cell designs that are made with plate lots that have high thickness increase rates, or certain other conditions might have sudden failure like this.

For others where this plate thickness doesn't become such a problem, such as shallow DOD and so forth, this might move out here somewhere.

And this other mechanism will be the end-of-life feature.

My point is that just looking at the voltage data from the satellites and seeing the lack of degradation, one should limit the euphoria from such a situation because there may be things going on that will suddenly become visible shortly after you have made the measurement.

DISCUSSION

HALPERT: You mentioned with the process you know and love you seem to get uniform impregnation. But you also mentioned the fact that you have to have a nice, uniform sinter.

Where, pray tell, do you get a plaque with a uniform sinter?

MAURER: I leave that as an exercise for the student.

TABLE I
SUMMARY OF TEST CONDITIONS

TEMP.

1. 0°
2. RT (23°C)
3. 45°

LOT

1. BTL - BTL ED PLATES
2. 9 - GE CD PLATES FROM COMSTAR LOT 9 CELLS
3. 12 - GE CD PLATES FROM COMSTAR LOT 12 CELLS
4. 19 - GE CD PLATES TO BE USED IN RECENT CELLS OF COMSTAR DESIGN

ELECTROLYTE COMPOSITION

1. 30% - 7M KOH }
2. 20% - 4M KOH }
3. CO₃ - 3.5 M KOH / 1.8 M K₂CO₃ (SIMULATES EFFECT OF NYLON DEGRADATION)
4. K/NA - 50% 7M KOH / 50% 10M NaOH (NA TO IMPROVE CHARGE EFFICIENCY)

TEST REGIME

1. 1A - C/6 CHG, C/2 DISCH; RECONDITION C/40 CONTINUOUS TO 0.6V
2. 1B - C/6 CHG, C/2 DISCH; RECONDITION C/40, 8 HRS ON/16 HRS OFF TO 0.6V
3. 2A - C/20 CHG, C/2 DISCH; }
4. 3A - C/6 CHG/C/30 CHG, C/2 DISCH; } RECONDITION SAME AS 1A

POSITIVE PLATE GROWTH DATA

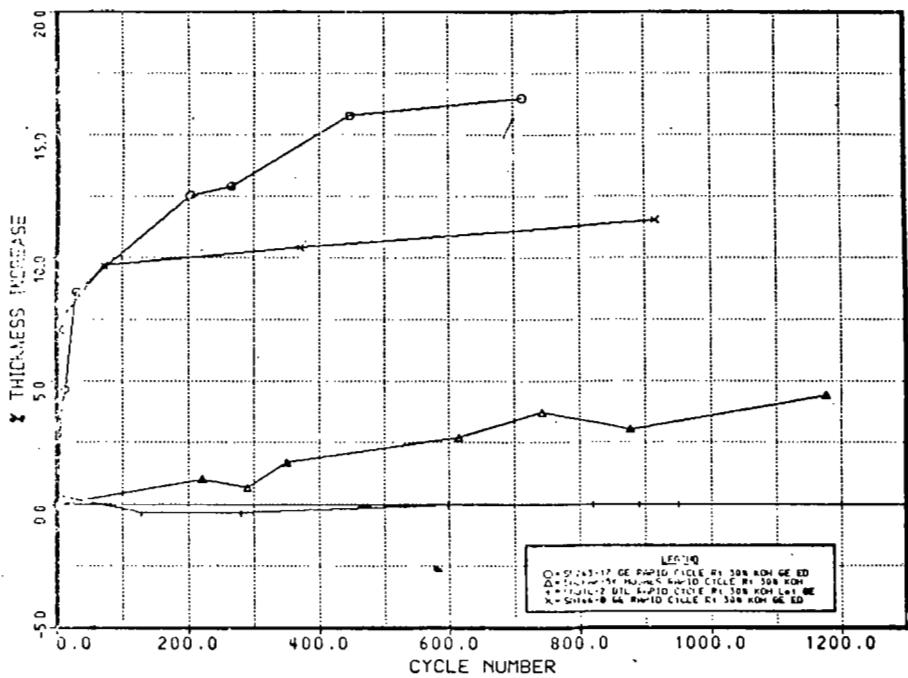


Figure 6-2

POSITIVE PLATE GROWTH DATA

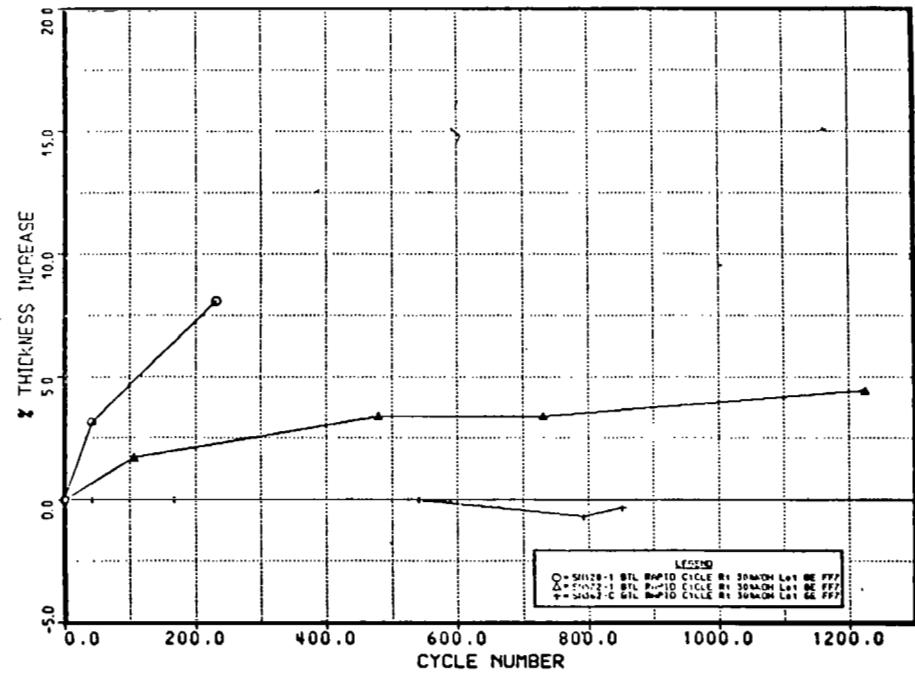


Figure 6-3

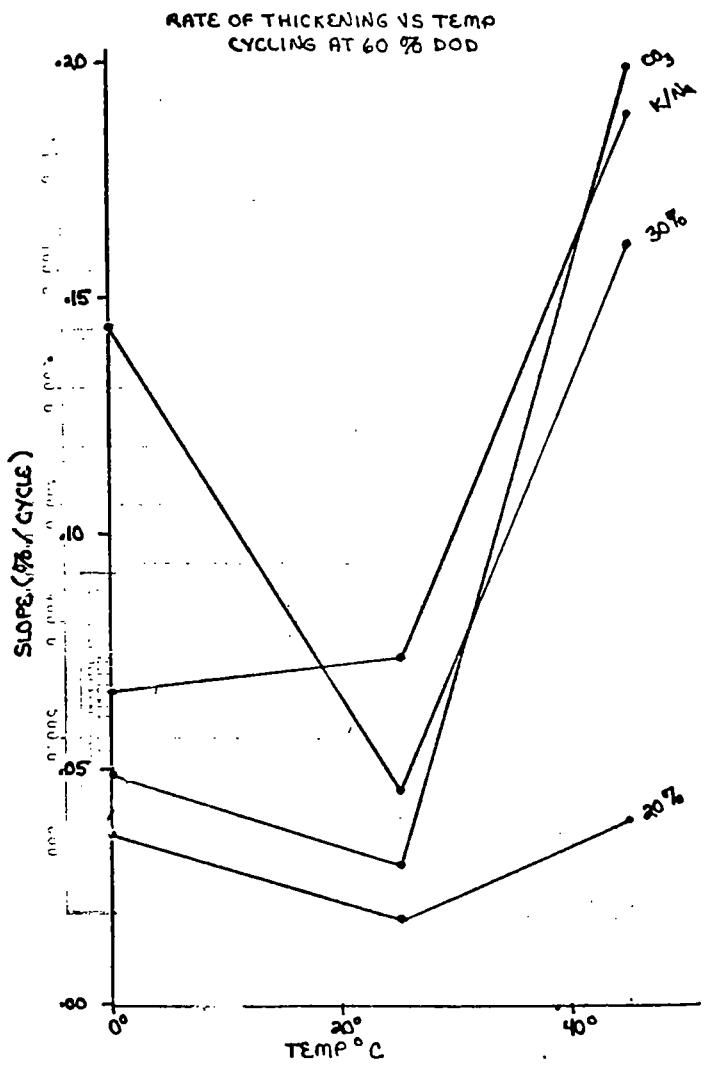


Figure 6-4

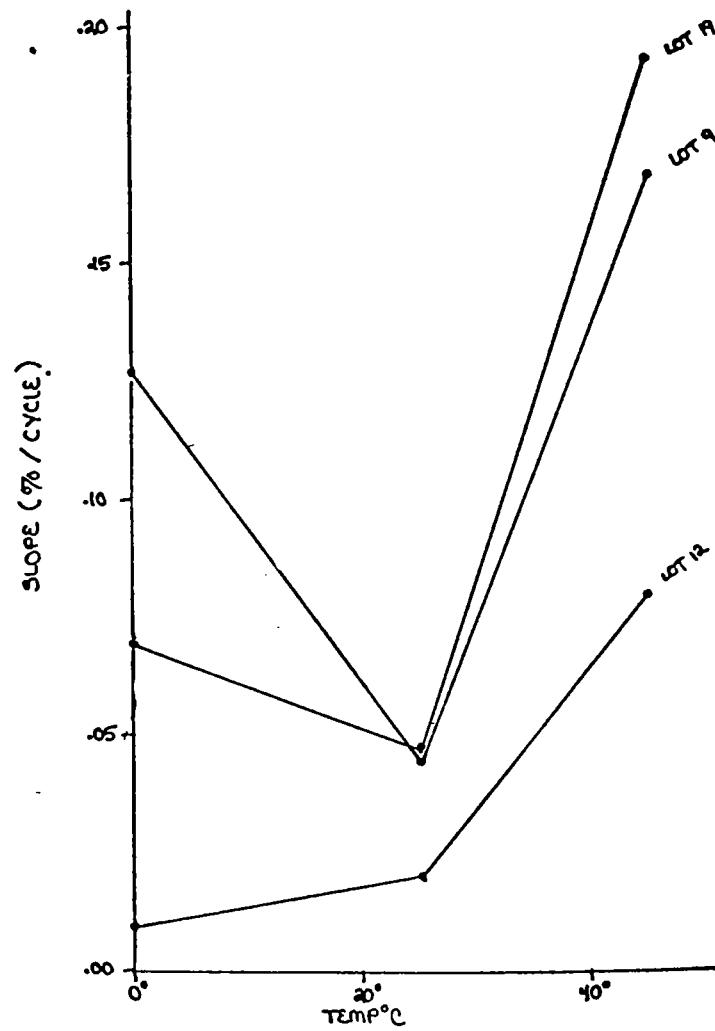


Figure 6-5

TABLE 2

Ratio of Thickening Rates at 23°C for Cycle Regime Pairs

<u>Regime Pair</u>	<u>Description</u>	<u>Ratio</u>
1B / 1A	Recondition 8Hrs on/16Hrs off Recondition Continuous	1.6
3A / 1A	C/6, 110% / C/30 Charge C/6, 110% Charge	3.0

Figure 6-6

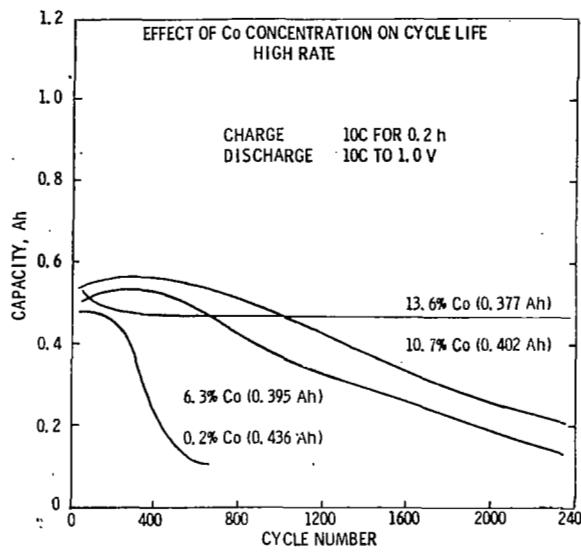


Figure 6-7

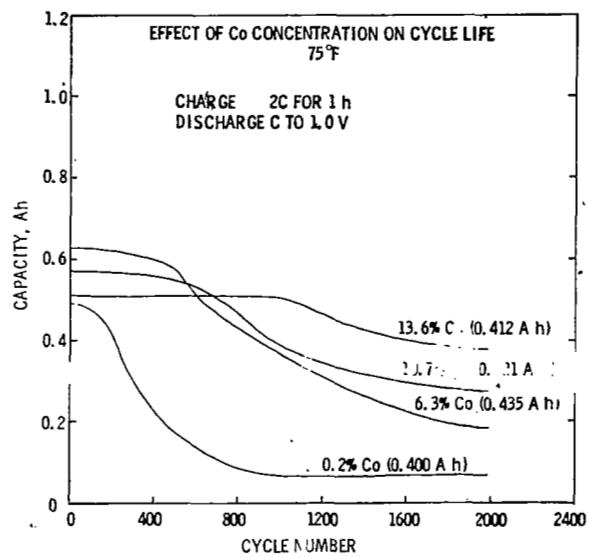


Figure 6-8

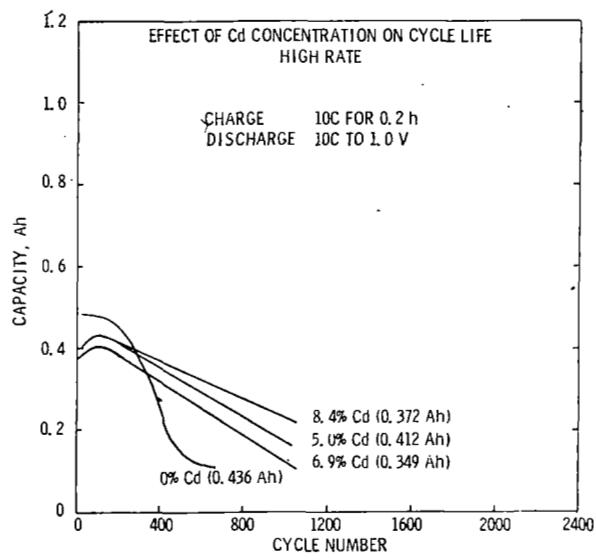


Figure 6-9

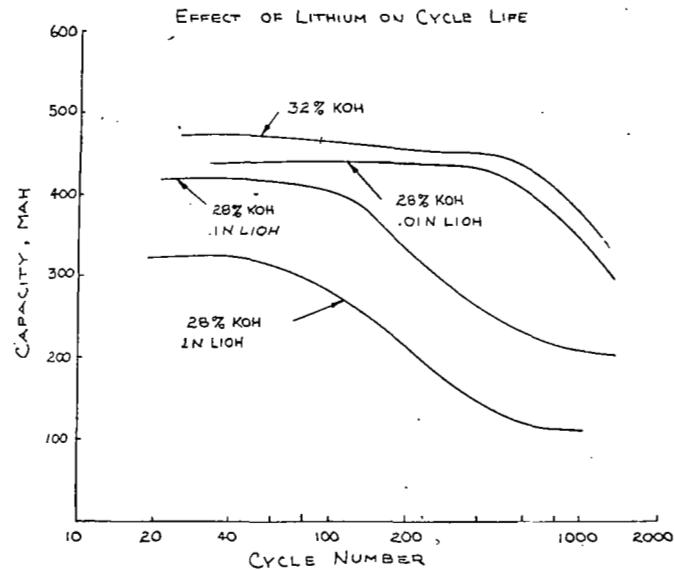


Figure 6-10

POSITIVE PLATE GROWTH DATA

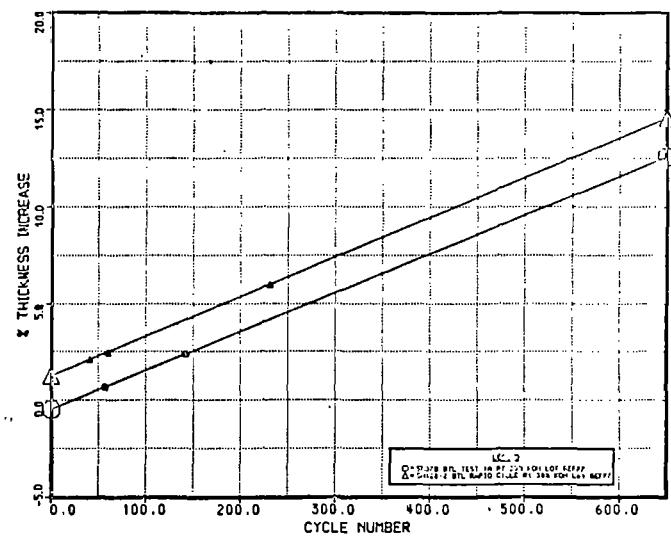


Figure 6-11

POSITIVE PLATE GROWTH DATA

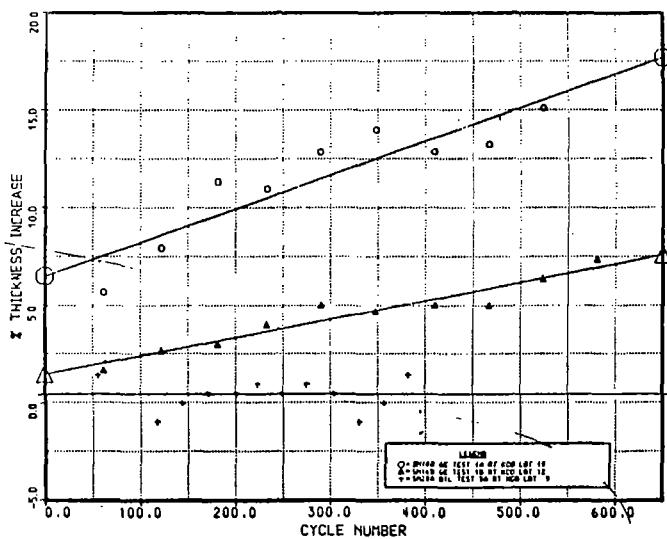


Figure 6-12

POSITIVE PLATE GROWTH DATA

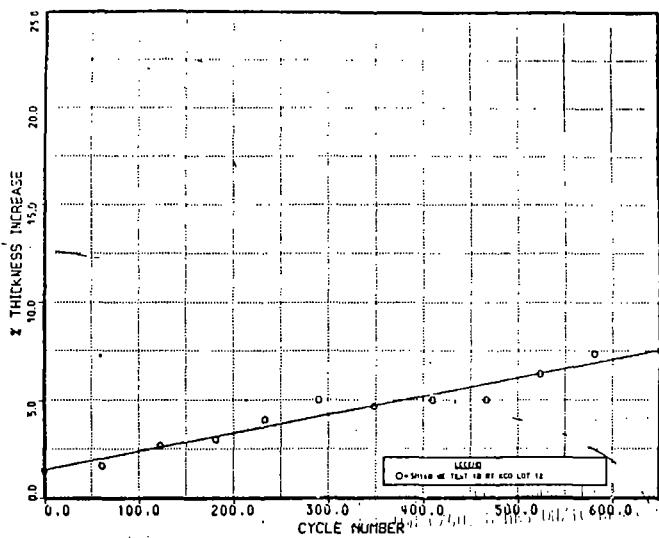


Figure 6-13

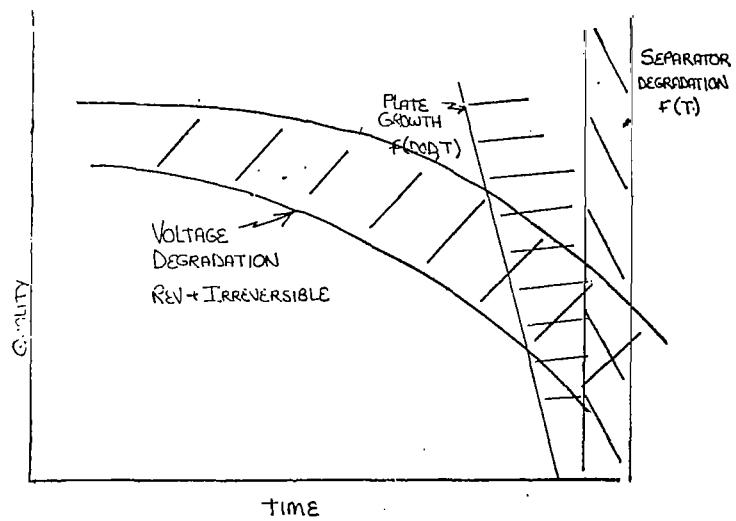


Figure 6-14